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Surface and interface magnetic structures of thin films studied by x-ray magnetic circular dichroism

T. Ohta[1], K.Amemiya[1] and D.Matsumura[1]

Summary

X-ray magnetic circular dichroism (XMCD) has been successfully applied to characterize the magnetic structures of thin films. It provides information of element specific magnetic spin and orbital moments and spin orientations. Newly developed depth-resolved XMCD makes possible to analyze the magnetization of surface and interfaces. Several typical applications of XMCD are demonstrated in this report.

Introduction

Discoveries of perpendicular magnetic anisotropy (PMA) [1] in layered structures and giant magnetoresistance (GMR) [2], exchange bias [3] effects have given a big impact both on magnetorecording industry and on basic science of magnetism. Now, some of them are used as commercial products, but their microscopic origins have not been clarified yet. It is intriguing to study the behavior of spins at the surfaces and interfaces and the effects of layer thickness and molecular adsorption on the spins in relation to the geometric structures.

To study the magnetic properties of layered or thin magnetic films, a number of methods have been developed, such as SQUID, Kerr effect, ferromagnetic resonance, neutron diffraction, magnetoresistance, AC-susceptibility, Brillouin scattering, magnetic dichroism, and Mössbauer effect.

Among them, X-ray magnetic circular dichroism (XMCD) has several unique advantages over other methods[4]. (1) Element specific information is obtained, since X-ray can tune the energy to a specific element. (2) Spin and orbital contributions can be discriminated by using the atomic sum rule. (3) Spin direction can be determined by changing the incident angle of x-rays, since the interaction between circular polarized x-rays and the photo-excited electrons is most enhanced when the x-ray incident direction is aligned to the magnetic moment of the electrons. (4) Surface magnetism can be probed with high sensitivity by using surface sensitive detection techniques. (5) An element specific hysterisis curve can be obtained, by fixing the photon energy at the L_3 edge of a specific element and sweeping the applied magnetic field.

[1]Department of Chemistry, Graduate School of Science, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Recently, we have used XMCD to investigate the spin reorientation transition induced by molecular adsorption and thickness of magnetic layers.

Spin reorientation transition induced by molecular adsorption

The magnetic anisotropy and the magnetic easy axis of thin films are influenced by gaseous adsorption on the surfaces[5] In addition, magnetization of the adsorbates is also induced by adsorption on the surface[6]. The sign of the magnetic coupling between adsorbates and thin films was found to be related to the magnetic easy axis of the films. These facts suggest that the magnetic anisotropy of thin films is affected by the adsorption of gaseous molecules.

Typical example of the spin reorientation transition is the case of Co/Pd(111) induced by CO chemisorption[7]. We studied this system by means of XMCD and XPS measurements[8]. XMCD provides information on a magnetization of the Co thin film. We found that quenching of the surface parallel magnetic orbital moment by CO adsorption is a key of PMA stabilization. On the other hand, XPS is a surface analytical method, sensitive to the chemical environment. For CO adsorption systems, their adsorption sites can be discriminated by the XPS chemical shift. Thus, we can examine the correlation between the CO surface adsorption fashion and the spin reorientation transition of Co thin films induced by stepwise CO adsorption and desorption. It is a new approach to observe magnetism of a thin film from the view of surface chemistry.

In order to check the magnetic easy axis of each thin film, XMCD measurements were performed at normal incidence (θ=90°) for the detection of perpendicular magnetization, and at grazing incidence (θ=30°) for the detection of the in-plane magnetization. For the clean Co/Pd(111) system, the region of PMA is below 3.5 ML. CO adsorption at 300 K does not shift the critical thickness of the Co/Pd(111) at all, while at 200 K, CO-covered films show a wider region of PMA than the clean one by about 3 ML. Co films with a thickness of 4-6 ML inherently show a parallel magnetic easy axis and undergo a spin reorientation transition from surface parallel to perpendicular direction upon CO adsorption at 200 K. These results indicate that PMA is stabilized by CO adsorption at 200 K but is not affected by that at 300 K.

In order to examine both the surface adsorption behavior of CO molecule and the change in magnetism of the Co thin film, C 1s XPS and Co L-edge XMCD spectra were measured at stepwise CO adsorption. Figure 1 shows the relationship between C 1s and Co XMCD spectra for the 4.5 ML Co film during CO dosage at 200 K. The Co film undergoes the spin reorientation transition from surface parallel (before CO adsorption) to perpendicular magnetization

(after completely covered with CO). Note that the x-ray incident angle was normal so as to detect only perpendicular magnetization for the XMCD measurements. Nearly zero XMCD signal during the low CO coverage indicates

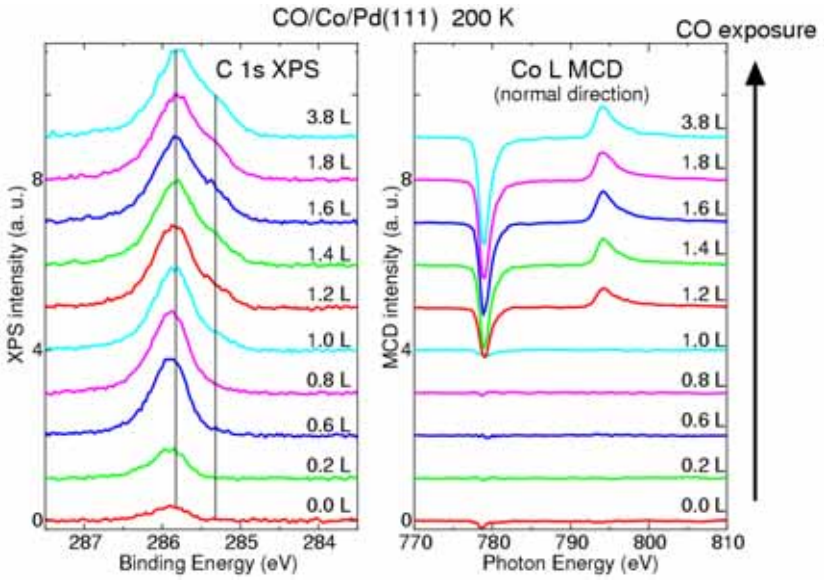

Fig. 1. C 1s photoemission spectra (left) and Co L-edge MCD spectra (right) from 4.6 ML Co/Pd(111) as a function of CO exposure. 1 L corresponds to the exposure of $1x10^{-6}$ Torr for 1 s.

that the Co thin film is fully magnetized in parallel direction before CO dosage, as confirmed by the XMCD observation at grazing incidence (not shown). The growth manner of the main XPS peak at 285.8 eV suggests the atop sites occupation at low coverages. At 1.0 L CO dosage, the main peak became saturated and a shoulder at 285.3 eV, which is assigned to a bridge site adsorption, gradually grew up. At the same time, Co XMCD gradually appeared, which means that the easy axis of Co has just begun to rotate the orientation of spin from surface parallel to perpendicular direction. At 1.8 L CO exposure, both C 1s and XMCD spectra were saturated, meaning that CO adsorption was completed and Co was fully magnetized perpendicularly. We found that the spin reorientation transition in Co/Pd(111) is induced as a consequence of CO adsorption on bridge site and not induced by CO adsorption on atop site which is the most energetically favored adsorption position. We have repeated these

adsorption and desorption experiments for several films which consist of 4-6 ML Co films on Pd(111) and observed similar behavior.

Surface and interface magnetic anisotropies of the thin films originate in structural and electronic effects. Some studies pointed out that the in-plane interatomic distance of a few ML Co films on Pd(111) seems to have a same distance with that of Pd due to the epitaxial growth. From the view of the structural effect, such an elongated interatomic distance at the interface creates the interface magnetic anisotropy. CO adsorption on the atop site does not affect the Co-Co interatomic distance so much, while CO atoms adsorbed at hollow or bridge site might push in the Co substrate and elongate the Co interatomic distance. It could be the reason why CO adsorbed on atop sites does not change the surface magnetic anisotropy while occupation of bridge or hollow sites creates the PMA.

We would like to emphasize that if one considers surface magnetic anisotropy of a thin film, it is important to know the surface structure of adsorbates. Because surface adsorption shows various structures under some conditions, these results allow us to have a new research field combining surface chemistry and magnetic thin films.

Depth-resolved XMCD

The magnetic depth profile of ultrathin films and multilayers has been extensively investigated, because the surface and interface often play important roles in the magnetic properties of actual materials. So far, such information has been obtained mainly by measuring the total magnetization as a function of film thickness, assuming that the magnetic properties at surface, interface, and inner layers are unchanged during the film growth [9]. However, this assumption is not always justified.

Recently, we have developed a simple but effective depth-resolved XMCD technique according to the following principle[10]. In the soft x-ray region, the x-ray absorption spectrum is obtained generally by counting the Auger electrons (and secondary electrons caused by them) emitted at the core hole relaxation, the number of which is proportional to the x-ray absorption intensity. The electron escape depth changes depending on the direction of emitted electrons. Therefore, the probing depth of the XMCD signal can be controlled by changing the electron detection angle. By using an imaging type MCP detector, all the spectra with various probing depths are recorded simultaneously. We applied this technique to Fe/Cu(100) and Fe/Ni/Cu(100) to directly investigate the magnetic depth profile.

Figure 2 shows Fe L-edge depth-resolved XMCD spectra from Fe/Ni/Cu(100) films taken at 200 K. All the spectra were recorded at grazing x-ray incidence (60º from normal), since these films exhibit the in-plane magnetization. It can be directly concluded that the Fe films have magnetically live surface layers in both cases. Interestingly, the surface of the 5 ML film has a negative magnetic

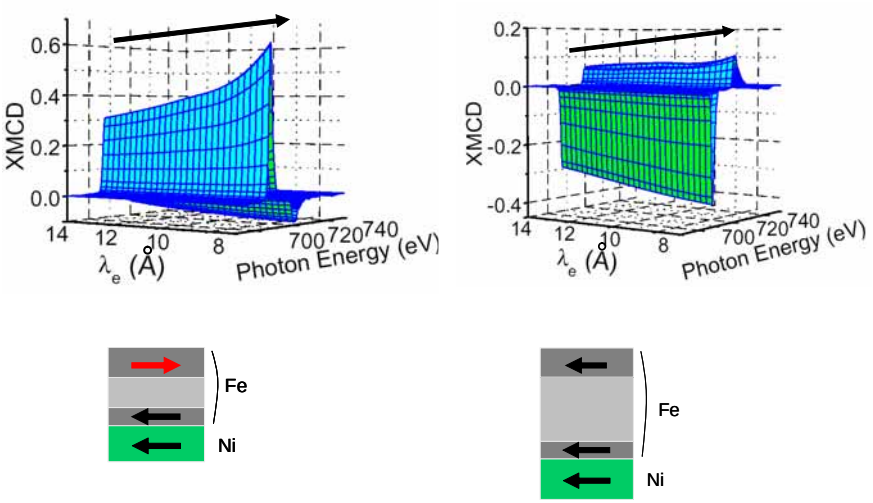

Fig. 2. A series of XMCD spectra from 5 ML Fe/Ni(10 ML)/Cu(001) (left) and 9 ML Fe/Ni(10 ML)/Cu(001). The arrows show the direction more surface sensitive. Spectra in the right side are more surface sensitive, as the electron escape depth is shorter. Bottom figures show the schematic representation of magnetic structures of these thin films.

moment, while the surface of the 9 ML Fe has a positive one. Here, the Ni film has a positive moment in both cases (spectra not shown). We have thus for the first time observed the surface magnetic layers and discovered some thickness dependent magnetic coupling between the Fe surface and Ni film.

This newly-developed depth-resolved XMCD can be applied to any thin film sample with atomic layer resolution. Magnetically live surface layers were unambiguously revealed with this technique. If the layer-by-layer analysis is possible, this method provides us model independent information of the magnetic depth profile. However, if a film were too thick to perform the layer-by-layer analysis, it is more reasonable to simulate the experimental results by using a model. As far as the model is based on the sound assumption and/or the results are confirmed by other experiments, it would provide us quantitative information

of the magnetic depth profile. Combination of this technique with the conventional thickness dependent measurement might be promising for the detailed analysis of depth profiling for complicated magnetic structures.

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